# A Novel Way To Synthesize Star Polymers in One Pot by ATRP of *N*-[2-(2-Bromoisobutyryloxy)ethyl]maleimide and Styrene

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ABSTRACT: A one-pot approach to synthesize star polymers by atom transfer radical polymerization (ATRP) of *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide (BiBEMI) with a large excess of styrene (St) was described. It was based on preferential consumption of BiBEMI, as an inimer, through its copolymerization with St, to form a branched intermediate in situ as the multifunctional core, which initiated homopolymerization of the excessive St to produce a star polymer. The kinetic studies exhibited two polymerization stages corresponding to the formation of the core with a faster propagating rate and the formation of arms by homopolymerization of St, respectively. $^1$H NMR spectra showed that in core formation stage random copolymer was formed. Analysis of the basic hydrolyzed products of the core by MALDI−TOF mass spectroscopy confirmed the branched structure of the core. A "6"-shaped polystyrene was also formed simultaneously, and its structure was confirmed by MALDI−TOF mass spectroscopy. Lowering the reaction temperature and using less excessive St could decrease the content of this polymer. Star polymers were characterized by $^1$H NMR, hydrolysis, and intrinsic viscosity.

## Introduction

Star polymer is a class of the simplest branched polymer that consists of multiple linear chains linked to a central core.[1] Because of its branched structure, star polymer often exhibits lower solution and melt viscosities compared to those of linear analogues of the same molar mass,[2] a characteristic that is very important for the applications, especially in fabrication processes of polymer materials. Star polymer also contains a higher degree of end-group functionalities, and this is quite important in many specialized applications. Because of these novel properties, star polymer has attracted considerable attention in recent years.

The preparation of well-defined star polymers was first reported by applying anionic living polymerization of vinyl monomers.[3] Cationic living polymerization was also used successfully in preparing star polymers since it was reported by Kennedy and co-workers.[4] Several recent reviews have summarized comprehensively on the syntheses of star polymers using anionic living polymerization[5] and cationic living polymerizations[6]. Employing ionic polymerizations, preparation of star polymers documented in the literature can be categorized into two approaches, namely the "arms first" and the "core first" methods.

In the "arms first" approach, the living linear arms of the star polymer were prepared first and then followed by polymerization of the arms with a small amount of a suitable multifunctional monomer, such as divinylbenzene[7] or ethylene glycol dimethacrylate,[8] to form a cross-linked microgel core and give the star polymer. It could also be achieved by coupling reaction of the reactive linear arm with a multifunctional linking agent with a defined number of quenching function,[9] whereas sometimes long reaction time was required and fractionation was needed to remove unreacted linear polymer to obtain pure star polymer.[5]

For "core first" approach, a multifunctional initiator as a core was synthesized first and then followed by polymerization of monomers to form the arms.[5] Accordingly, the number of arms can be controlled by the number of functionalities, and a well-defined star polymer with narrow molecular weight distribution can be obtained. However, in many cases the multifunctional initiators must be presynthesized, and limited studies[6b,10] employing ionic polymerizations have been documented using this method due to the poor solubility of multiply charged species needed to initiate ionic polymerizations.

Although a variety of star polymers have been prepared by living ionic procedures,[5,6b] the rigorous reaction conditions and monomer selections limit the applicability of this strategy. In contrast, controlled radical polymerization (CRP) has become a powerful tool in preparation of well-defined star polymers during the latest few years because it can overcome these limitations.[11−14] CRPs are often referred to atom transfer radical polymerization (ATRP)[11] or metal-catalyzed living-radical polymerization,[12] nitroxide-mediated polymerization (NMP),[13] and reversible addition−fragmentation chain transfer (RAFT)[14] polymerization. Using the arm first approach, star polymers were prepared by CRP,[15] but many reaction parameters may influence the structure of the resulting star polymers. This deficiency has been overcome by high-throughput combinatorial techniques in NMP.[16] The core first approach is the most frequently used method in the preparation of star polymers by CRP. Various families of initiators with defined number of functionalities were designed to serve as the central cores, and stars of polystyrene, poly(alkyl methacrylate), and poly(alkyl acrylate) as well as block copolymers were prepared. Several groups, for example, Matyjaszewski,[11,17] Sawamoto,[12,18] Hawker,[13,19] Miller,[20] Gnanou,[21] Haddleton,[22] Pan,[23] and Rizzardo,[24] have contributed much to this area. No matter which approach was used in preparation of star polymers in the literature, either the core

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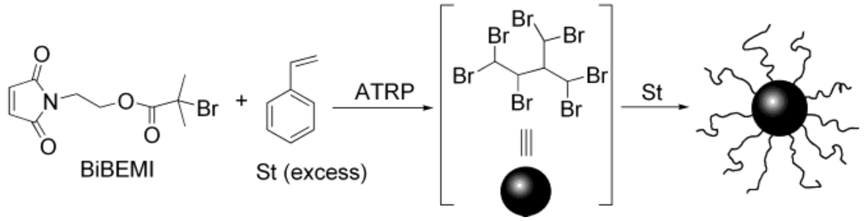
**Scheme 1**



or the arms should be synthesized in a separate step; at least chemicals were added step by step. That is to say that two steps are needed to get a star polymer. It may bring problems in industrial preparation. Therefore, a simple way of synthesis is highly appreciated.

This paper reports a novel one-pot approach to prepare star polymers by ATRP. The strategy is based on ATRP of BiBEMI and St (Scheme 1). When excess St is used, preferentially copolymerization of BiBEMI, as an inimer, with St may be expected through charge-transfer complex (CTC)[25] and give an intermediate, which is supposed to be a branched structure, by self-condensing of vinyl polymerization (SCVP).[26] Once the inimer is consumed, a multifunctional core is formed in situ, and grafting polymerization of the excessive St from the core as an initiator may proceed to form a star polymer. When this paper was under submission, another example of one-pot strategy was reported by Ishizu and co-workers using a system of free radical photopolymerization applying a similar principle.[27] In their system, polymerization of excessive methyl methacrylate, inimer (*N*,*N*-diethyldithiocarbamyl)methylstyrene, and 4,4′-bismaleimidediphenylmethane in benzene under UV irradiation was studied.

## Experimental Section

**Materials.** *N*-(2-Acetoxyethyl)maleimide (AEMI), mp 78.5−79.5 °C (lit. mp 79 °C), and CuBr were prepared according to the literature.[28,29] Styrene was stirred over $CaH_2$ overnight and distilled under reduced pressure. Triethylamine was dried by KOH. Tetrahydrofuran (THF) and dioxane were distilled over Na prior to use. Anisole was washed with 10% NaOH solution and dried by $CaCl_2$ and distilled before use. 2-Bromoisobutyryl bromide (98%, Aldrich), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich), and other reagents were commercialized chemicals and used as received.

**Measurement.** Monomer conversion was determined by a Beifen model SQ204 gas chromatograph (GC) equipped with a FID detector using a 25 m capillary column; dioxane or anisole was used as internal standards. Gel permeation chromatography (GPC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4) using THF as eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for the calibration. $^1H$ NMR spectra were recorded on a Varian 300 MHz spectrometer in $CDCl_3$ at room temperature. Matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Both matrix 4-hydroxy-α-cyanocinnamic acid (CCA) and sample were dissolved in 1:1 (v/v) acetonitrile:water with 1% trifluoroacetic acid. 0.5 $\mu$L of this mixture solution was placed on a metal sample plate and air-dried at ambient temperature. Mass spectra were acquired in positive reflector mode using an acceleration voltage of 19 kV. External mass calibration was performed using a standard peptide mixture. Spectra were obtained by setting the laser power close to the threshold of ionization, and generally 100 pulses were acquired and averaged. Static light scattering (SLS) experiments were carried out on a ALV DLS/SLS-5022F instrument using a He−Ne laser ($\lambda_0 = 632.8$ nm). Prior to the light scattering measurements, the sample solution was centrifuged with a velocity of 12 000 rpm and then filtered using filters with a pore size of 0.2 $\mu$m. The refractive index increment (d*n*/d*c*) of polySt was used as that of the star polymer because the content of BiBEMI unit in the polymer is not more than 4% calculated from the conversion of St. Intrinsic viscosity was measured by an Ubbelohde-type capillary viscometer in toluene at 35 °C.

**Synthesis of *N*-(2-Hydroxyethyl)maleimide.** AEMI (9.15 g, 50 mmol) and *p*-toluenesulfonic acid hydrate (0.915 g, 4.8 mmol) were dissolved in a 180 mL mixture of methanol and water (volume ratio, 5:1). The solution was allowed to reflux for 72 h, and then methanol and water were evaporated. The crude product was purified by recrystallization in methanol to give the title compound as a white crystal: 5.71 g (yield, 81%); mp 71.5−72.5 °C (lit. mp 70−71 °C).[28] $^1H$ NMR ($CDCl_3$): $\delta$ (ppm): 2.02 (s, 3H, $-CO-CH_3$), 3.80 (t, 2H, $=N-CH_2-$), 4.22 (t, 2H, $-CH_2-O-$), 6.73 (s, 2H, $-CH=CH-$).

**Synthesis of BiBEMI.** 2-Bromoisobutyryl bromide (3.4 mL, 27.6 mmol) was added dropwise to the mixture of *N*-(2-hydroxyethyl)maleimide (3.24 g, 23 mmol) and dry triethylamine (5 mL, 34 mmol) in 60 mL of THF at 0 °C for 1 h. The mixture was stirred for 4 h at 0 °C and at room temperature for 38 h. The triethylammonium bromide was removed by filtration, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography using 1:5 (volume ratio) ethyl acetate/petroleum ether as eluent to obtain the title compound: 4.58 g (yield, 69%); mp 64.5−65.5 °C. $^1H$ NMR ($CDCl_3$): $\delta$ (ppm): 1.89 (s, 6H, $-C(Br)-CH_3$), 3.86 (t, 2H, $=N-CH_2-$), 4.34 (t, 2H, $-CH_2-O-$), 6.74 (s, 2H, $-CH=CH-$). Elemental analysis: Calcd for $C_{10}H_{12}BrO_4N$: C, 41.40; H, 4.17; Br, 27.54; N, 4.83. Found: C, 41.82; H, 4.22; Br, 28.26; N, 4.85.

**Synthesis of Star Polymers.** A typical procedure is as follows: In a 25 mL Schlenk flask, CuBr (0.058 g, 0.4 mmol) was purged three times with $N_2$, and then deoxygenated PMDETA (0.084 mL, 0.4 mmol) was added. Afterward, a deoxygenated mixture of St (4.6 mL, 40 mmol), BiBEMI (0.232 g, 0.8 mmol), and dioxane (2.3 mL) was transferred to the flask, and the flask was placed in an oil bath at 80 °C with stirring. Samples with different time intervals were taken to analyze St conversion by GC and monitor the polymerization by GPC. The catalyst was removed by passing through a basic alumina column prior to GPC analysis. The samples for $^1H$ NMR analysis were precipitated from petroleum ether (boiling range 60−90 °C) and dried under vacuum.

**Hydrolysis of the Star Polymer.** A typical procedure is as follows: The star polymer (0.3 g) in THF (40 mL) and KOH ethanol solution (1 M, 30 mL) were mixed and refluxed for 72 h. The solution was neutralized by dilute hydrochloric acid and then evaporated to dryness. The residue was dissolved in THF, and insoluble material was removed by filtration.

## Results and Discussion

**Polymerization Kinetics.** Figure 1 shows ATRP of BiBEMI and St in dioxane at 80 °C. The plot of $\ln([M]_0/[M])$ against polymerization time seems to be composed of two stages. During the period of initial 30 min, the apparent propagation rate constant ($k_p^{app}$) is obviously larger than that of the later period. The $k_p^{app}$(bulk, 80 °C) $= 3.3 \times 10^{-4}\ s^{-1}$ of copolymerization of St and AEMI estimated from kinetic studies given in the literature[25a]

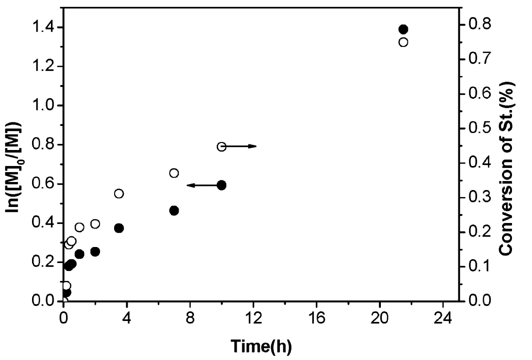


**Figure 1.** Kinetic plot of the copolymerization of BiBEMI with St by ATRP. $[BiBEMI]_0:[St]_0:[CuBr]:[PMDETA] = 1:50:0.5:0.5$, at 80 °C in dioxane; $V_{dioxane}:V_{St} = 1:2$.

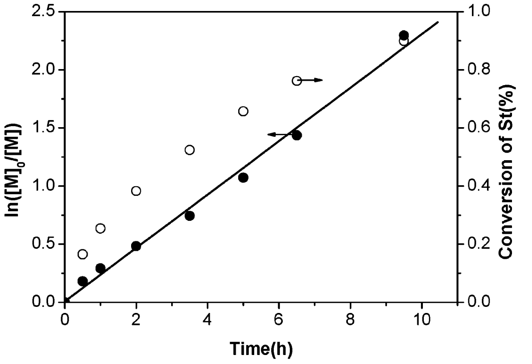


**Figure 2.** Kinetic plot of the copolymerization of BiBEMI with St by ATRP. $[BiBEMI]_0:[St]_0:[CuBr]:[PMDETA] = 1:50:0.5:0.5$, at 100 °C in anisole; $V_{anisole}:V_{St} = 1:2$.

is bigger than the $k_p^{app}$(bulk, 110 °C) $= 1.6 \times 10^{-4}$ s$^{-1}$ of homopolymerization of St reported by Matyjaszewski[30] under similar ATRP conditions. Also, the propagation rate constant of alternating copolymerization by conventional radical polymerization is much faster than that of homopolymerization of vinyl monomers, for example, St.[31] In present study, when excess St was present, the inimer, BiBEMI, should be preferentially consumed by copolymerization with St at a much faster rate, and an intermediate in the initial stage was expected to form. This stage took less than 30 min under present conditions. From this intermediate as a core, homopolymerization of St would proceed at a lower rate in a second stage.

But the two stages were not observed when the polymerization temperature was 100 °C in anisole. Figure 2 shows that the plot of ln([M]$_0$/[M]) against polymerization time is linear. The $k_p^{app}$ ($6.47 \times 10^{-5}$ s$^{-1}$) is bigger than $k_p^{app}$ ($1.51 \times 10^{-5}$ s$^{-1}$) calculated from the second stage of the plot in Figure 1. Thus, the polymerization under 100 °C was much faster than that under 80 °C, and the consumption of BiBEMI might be finished in a short time under higher temperature. Therefore, the initial stage "disappears" from the plot, and the observed straight line may be attributed to the homopolymerization of St from the core. The two stages were not observed in Ishizu's system.[27]

GPC traces of kinetic samples taken from two polymerizations are illustrated in Figures 3 and 4. These figures show that the peaks of main proportion in higher molecular direction are broad at the early stage of copolymerization but changed to overlapped multipeaks with the increase of polymerization time. This change may be explained by the molecular mass difference

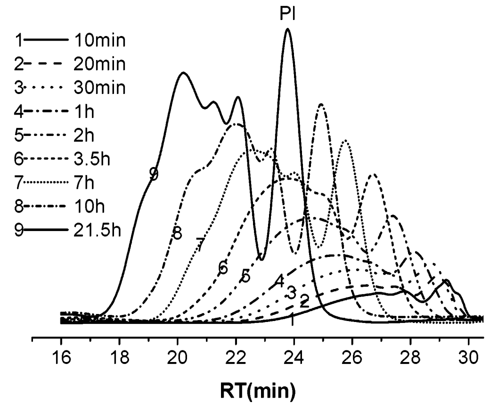


**Figure 3.** GPC traces of the copolymerization of BiBEMI with St by ATRP. $[BiBEMI]_0:[St]_0:[CuBr]:[PMDETA] = 1:50:0.5:0.5$, at 80 °C in dioxane; $V_{dioxane}:V_{St} = 1:2$.

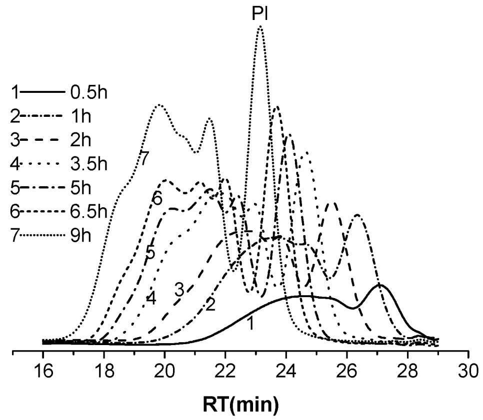


**Figure 4.** GPC traces of the copolymerization of BiBEMI with St by ATRP. $[BiBEMI]_0:[St]_0:[CuBr]:[PMDETA] = 1:50:0.5:0.5$, at 100 °C in anisole; $V_{anisole}:V_{St} = 1:2$.

before and after grafting arm chains. The core, the branched oligomer copolymers, had a broad distribution, and the molar mass differences were not big. However, because of the arm grafting, the molar mass differences between the stars with different number of arms became much larger and overlapped curves became obvious. In the low molecular weight region, there was a monomodal peak, Pl, with a small $M_w/M_n$ (<1.2). Analysis of the samples from other polymerizations with different conditions showed that different solvents and temperatures had no great effect on the contour of every curve, except the relative area of Pl to the main composition.

Samples taken with different time intervals were analyzed by $^1$H NMR spectroscopy, which are shown in Figure 5. For comparison, a linear alternating copolymer of BiBEMI and St was synthesized by traditional free radical polymerization using AIBN as initiator. Its $^1$H NMR spectrum (Figure 6) gave a strong signal, a, between $\delta$ 1.7 and 2.0 ppm due to the protons of the $-C(CH_3)_2Br$ groups. The two peaks, b and c, between $\delta$ 3.5 and 4.5 ppm are attributed to the $-NCH_2CH_2O-$ groups in the linear structure. The broad peak around $\delta$ 5.8−7.5 ppm in Figure 6 is the signal of the phenyl protons. In Figure 5, the strong peak in the upfield ($\delta$ 0.6−1.2 ppm, region 1) is due to $-OCOC(CH_3)_2-C-$ groups, indicating $-OCOC(CH_3)_2Br$ groups have been transformed to $-OCOC(CH_3)_2-C-$ groups by initiating ATRP.[32] The peak between $\delta$ 3.0 and 4.0 ppm (region 2 in Figure 5) is attributed to the $-NCH_2CH_2O-$ groups. These differences in Figures 5 and 6 showed that the structure of the polymer formed in the initial stage was

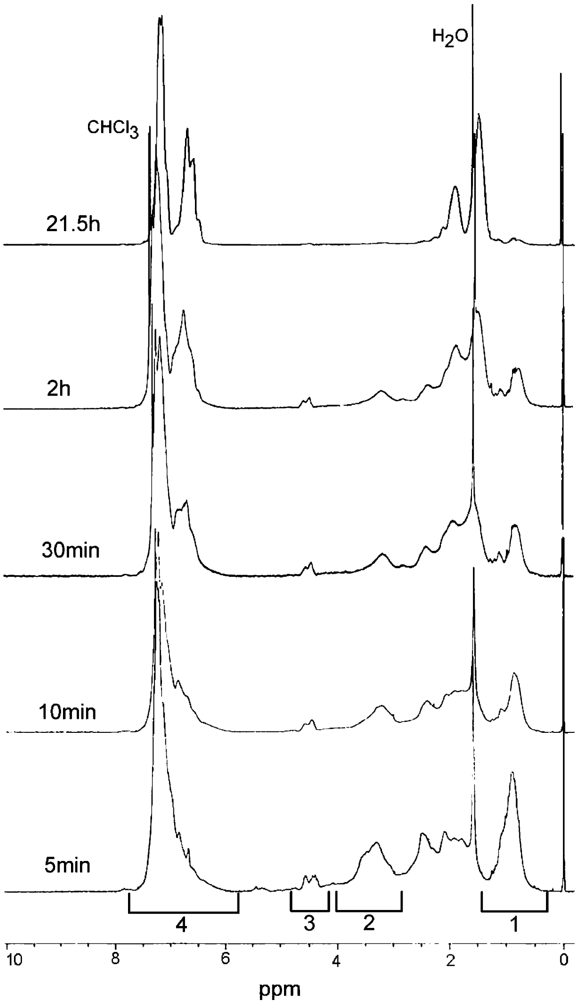


**Figure 5.** $^1$H NMR spectra of the polymers in different reaction times from the polymerization as in Figure 1.

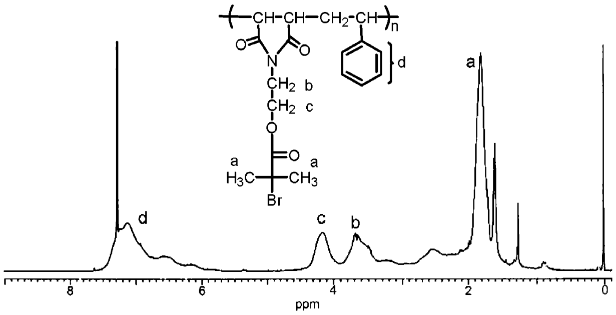


**Figure 6.** $^1$H NMR spectrum of a linear alternating copolymer of BiBEMI and St synthesized in chloroform at 60 °C using AIBN as initiator ($M_n = 2.2 \times 10^5$, $M_w/M_n = 2.2$ by GPC). Its alternating structure was proved by elemental analysis results. The molar ratio of the two monomer units in the copolymerization products at low conversions was always close to 1:1 when the molar feed of BiBEMI:St changed from 1:3, 1:2, 1:1, 2:1, to 3:1.

**Table 1. Increment of the Molar Ratio of St to BiBEMI Units ($r_{S:B}$) in the Polymer during the Polymerization**[a]

| reaction time | conv of St (%)[b] | $r_{S:B(th)}$[c] | $r_{S:B(NMR)}$[d] |
|---|---|---|---|
| 5 min | | | 2.7 |
| 10 min | 7 | 3.5 | 3.7 |
| 30 min | 13 | 6.5 | 7.5 |
| 1 h | 17 | 8.5 | 9.8 |
| 2 h | 23 | 11.5 | 12.8 |
| 10 h | 45 | 22.5 | 21.6 |
| 21.5 h | 75 | 37.5 | 36.7[e] |
| | 100 | 50 | |

[a] $[BiBEMI]_0:[St]_0:[CuBr]:[PMDETA] = 1:50:0.5:0.5$, at 80 °C in dioxane; $V_{dioxane}:V_{St} = 1:2$. [b] Determined by GC. [c] Calculated from conversion of St: $r_{S:B(th)} = 50 \times$ conversion of St/1. [d] Calculating from areas of region 4 and region 2 in Figure 5: $r_{S:B(NMR)} =$ (area of region 4/5):(area of region 2/4). [e] (Area of region 4/5):(area of region 1/6).

different from the linear alternating polymer, revealing that the main structure of the initially formed polymer was unlikely to be a linear alternating copolymer. The proportion of $-OCOC(CH_3)_2-C-$ structure is 86% calculated from [(area of region 1)/6]/[(area of region 2)/4], and that of $-OCOC(CH_3)_2Br$ is deduced to be 14%. That is to say, at the polymerization time of 5 min, 86% of the $-OCOC(CH_3)_2Br$ groups were transformed to the $-OCOC(CH_3)_2-C-$ structure, and 14% still existed in the polymer. The broad and strong peak around $\delta$ 6.0–7.5 ppm (region 4 in Figure 5) is ascribed to the phenyl protons of St units. Along with the increase of the reaction time and conversion of St, the shape of this peak gradually changed to a typical shape of pure polySt, indicating the structure of the initially formed polymer was different from the polymer formed afterward. The peaks between $\delta$ 4.3 and 4.7 ppm (region 3 in Figure 5) are ascribed to the protons attached to the $\omega$-end group, $C-CH-Br$, and its intensities decrease gradually with the time. The above observations demonstrate that there were polySt chains with terminal Br produced in ATRP. The small sharp peak at $\delta$ 6.7 ppm in the polymer given at 5 min is the protons of the $\alpha$-end vinyl groups from maleimide moieties, and this peak is overlapped by the phenyl protons in polySt. From these spectra, the molar ratio of St to BiBEMI units ($r_{S:B(NMR)}$) in the polymers was calculated as listed in Table 1. The theoretical values were calculated from the conversion of St assuming that all the BiBEMI were consumed and contained in the polymers. The observed $r_{S:B(NMR)}$ agrees well with the theoretical value $r_{S:B(th)}$. The $r_{S:B}$ value reaches nearly 3 at 5 min of polymerization and increases greatly with the time. This result demonstrates that the copolymerization of two monomers in the core formation stage did not give strictly alternating structure and the core formation was earlier than St homopolymerization. The random copolymerization in core formation stage is not difficult to understand because the feed ratio of St to BiBEMI is very large.

**Formation and Structure of the Core.** The core of the star polymer is proposed to originate from the copolymerization of BiBEMI, the inimer, and St in a similar way as SCVP of AB* type monomer studied in the literature.[26b,c] Its random copolymerization has been proved in the former section since a large excess of St was used. Two kinds of structures A* and B* (shown in Scheme 2) could act as chain propagation points. The possible structures of the initially formed polymers may be categorized roughly into three types, as shown in Scheme 2. Type **a** is given by vinyl propagation only at the A* points while B* is less active, and type **b** is formed when only B* acts as radical addition propagation point. These two types are linear polymers in the extreme cases. If both A* and B* act as propagation points, type **c**, the branched structure can be formed. Of course, no matter which structure of **a**, **b**, or **c** is the core, star polymer may be produced since the core bears multifunctionalities and if polySt branches are long enough. As discussed above, $^1$H NMR spectra (Figure 5) show that the polymer formed in the initial stage is

**Scheme 2**

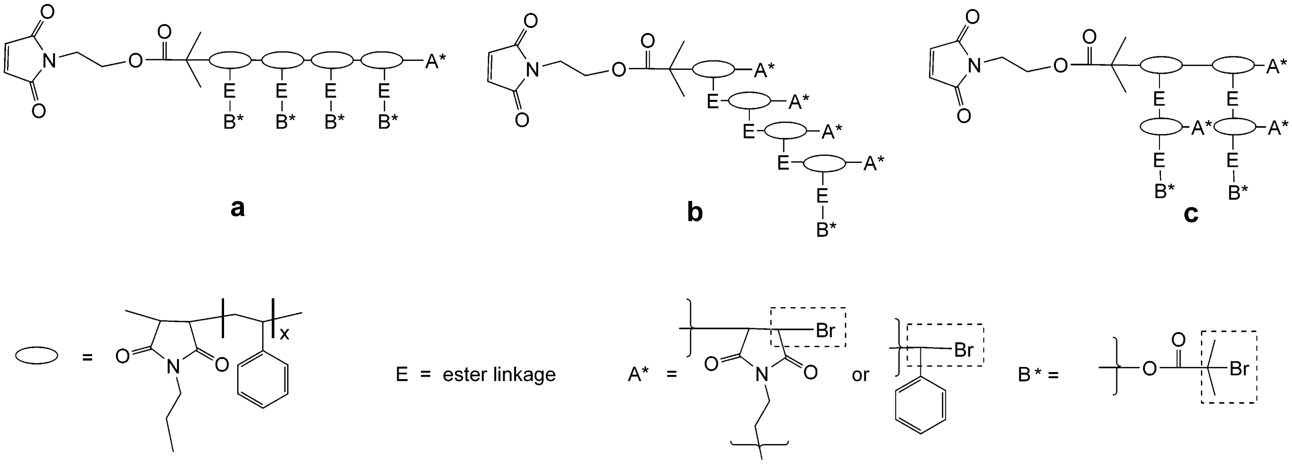
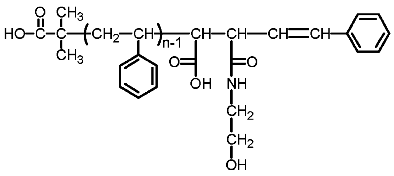
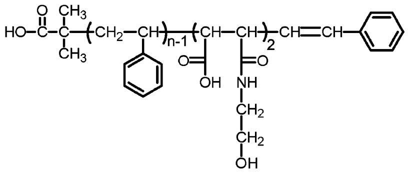
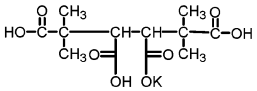
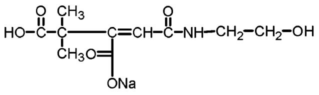


**Table 2. *m/z* Values of Main Peaks in the MALDI−TOF Mass Spectrum (Figure 7) and Their Corresponding Molecular Structures**

| Mass series | Molecular Structure (M) | Peak m/z values | Ion type |
|---|---|---|---|
| A |  | 476.2(n=2);580.2(n=3);<br>684.2(n=4);788.3(n=5) | M + Na$^+$ |
| | | 492.2(n=2);596.1(n=3);<br>700.2(n=4);804.2(n=5) | M + K$^+$ |
| B |  | 739.2(n=3);843.2(n=4);<br>947.3(n=5);1051.5(n=6) | M + Na$^+$ |
| | | 755.2(n=3);859.2(n=4);<br>963.3(n=5);1067.3(n=6) | M + K$^+$ |
| C |  | 366.4 | M + K$^+$ |
| D |  | 290.4 | M + Na$^+$ |

quite different from the linear alternating copolymer of BiBEMI and St synthesized by conventional radical polymerization. So the first linear structure, **a**, may be excluded. But $^1$H NMR cannot distinguish **b** and **c** since the signal of the protons of B* was overlapped by the protons from the main chain. From Scheme 2, one may note that there are ester groups inherited from the inimer in the structure. For **b**, every BiBEMI unit, with some St units, is separated by one ester group. Cutting ester group by hydrolysis may give fragments of one BiBEMI unit with a few St units. For **c**, because of branching, hydrolysis may give the pieces of at least two BiBEMI units with a few St units.

The polymer formed in the core forming stage at a reaction time of 5 min was thus hydrolyzed under basic conditions. The hydrolysis product was then analyzed by MALDI−TOF mass spectroscopy. Under the basic hydrolysis, the linear and branched polymer, **b** and **c**, could be broken into small molecules with carboxyl acid groups. The imide rings were opened simultaneously, but the resulted amide bonds were difficult to undergo further transformation to carboxyl acid.[33] The end bromine connected to the second carbon atoms may be removed by elimination of bromine hydride during the hydrolysis process.

The mass spectrum of the hydrolysis products is shown in Figure 7. Although the mass spectrum is complex due to the variety of hydrolysis products, the peaks with relatively high intensity still can be assigned to the structures in Table 2 with a deviation less than 1 Da between the observed masses and the calculated values, and the observed isotopic distributions also agree very well with the simulated ones.[34] The mass series A and B with a mass interval of 104 corresponding to the molar mass of St can be easily determined to be from the original polymer formed by random copo-

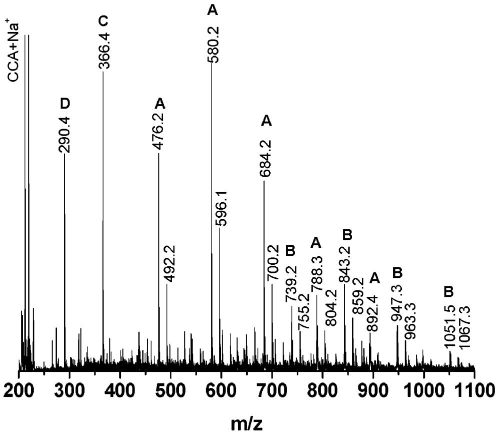


**Figure 7.** MALDI−TOF mass spectrum of the hydrolysis product of the polymer from the polymerization as shown in Figure 1 with reaction time of 5 min.

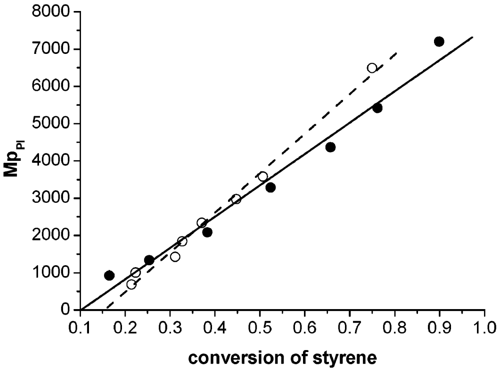


**Figure 8.** Peak molecular weight of Pl against conversion of St in the copolymerization of BiBEMI with St by ATRP. $[BiBEMI]_0$:$[St]_0$:[CuBr]:[PMDETA] = 1:50:0.5:0.5 (○, at 80 °C in dioxane; ●, at 100 °C in anisole).

lymerization of BiBEMI and St. The actual sequence of the BiBEMI and St units in the polymer may be different from the listed structures, but the composition is kept the same. Thus, series B in Table 2 originates from branch structure of the core, structure **c**. Series A may originate from **b** or from a segment of the branched core. The branched core is thus demonstrated although the actual core structure may be very complicated. The grafting polymerization from the initiating sites, A* and B*, of the core may generate the arms of the star polymers.

**Structure of Pl.** To explore the origin of Pl, plots of peak molecular weights ($M_p$) of Pl (shown in Figures 3 and 4) against conversion of St are shown in Figure 8. It is interesting to observe that both plots can be fitted linearly rather well. This result, also from kinetic studies in Figures 1 and 2, reveals the controlled polymerization nature for Pl. To identify its structure, Pl was fractionated from the polymerization product with reaction time of 2 h under the same polymerization conditions as listed in Figure 1. GPC curves of the product and Pl fraction are shown in Figure 9. Pl was first subjected to hydrolysis under basic conditions, and no difference was noticed as revealed by GPC analysis. It means the main chain is stable against hydrolysis. Both P1 and its hydrolysis products were then analyzed by MALDI−TOF mass spectroscopy, which gave results presented in Figure 10. From the mass spectrum of Pl (Figure 10I), a series of peaks with a mass interval of 104 between adjacent peaks, which corresponds to the molar mass of St, are observed. The series of peaks may be attributed to structure **a** or **b** shown in Scheme 3 since they have the same molecular weights. The calculated molar masses from the formulas agree very well with the experimental ones, and the elimination of HBr is also observed.[21c,35] The simulated and the observed isotopic distributions also agree very well for each main peak. But the structure **a** and **b** cannot be distinguished in Figure 10I. Structure **a** may be produced by ATRP of St with BiBEMI as an initiator while **b** may be given in a similar way but its maleimide end group copolymerized with St by tail biting of its own. As shown in Scheme 3, hydrolysis products of **a** and **b** are **a′** and **b′**, respectively, which have different molar masses and can be distinguished by mass spectroscopy. As shown in Figure 10II, the main series of the peaks labeled can be clearly attributed to structure **b′** in Scheme 3, which is given by **b**. The attribution of other peaks with relatively high intensity in Figure 10II could

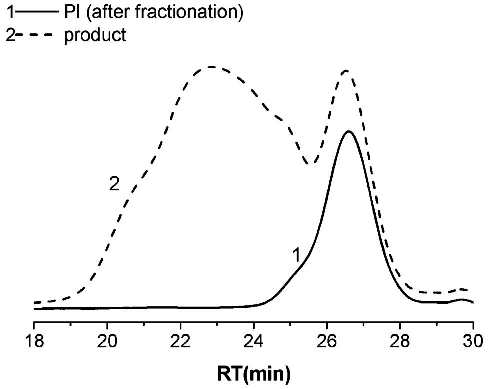


**Figure 9.** Pl fraction from the polymerization product. $[BiBEMI]_0$:$[St]_0$:[CuBr]:[PMDETA] = 1:50:0.5:0.5, at 80 °C in dioxane; $V_{dioxane}$:$V_{St}$ = 1:2; Pl: $M_n$ = 1500, $M_w/M_n$ = 1.15 by GPC.

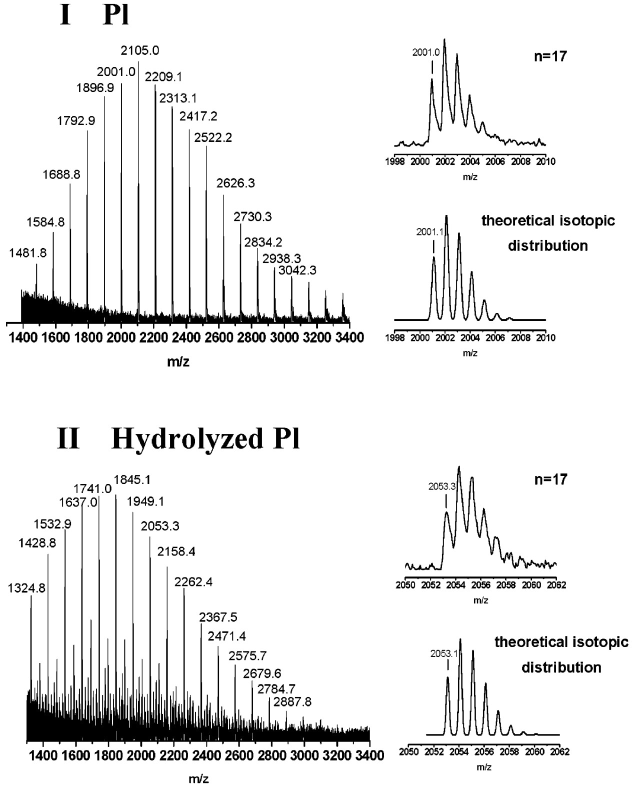
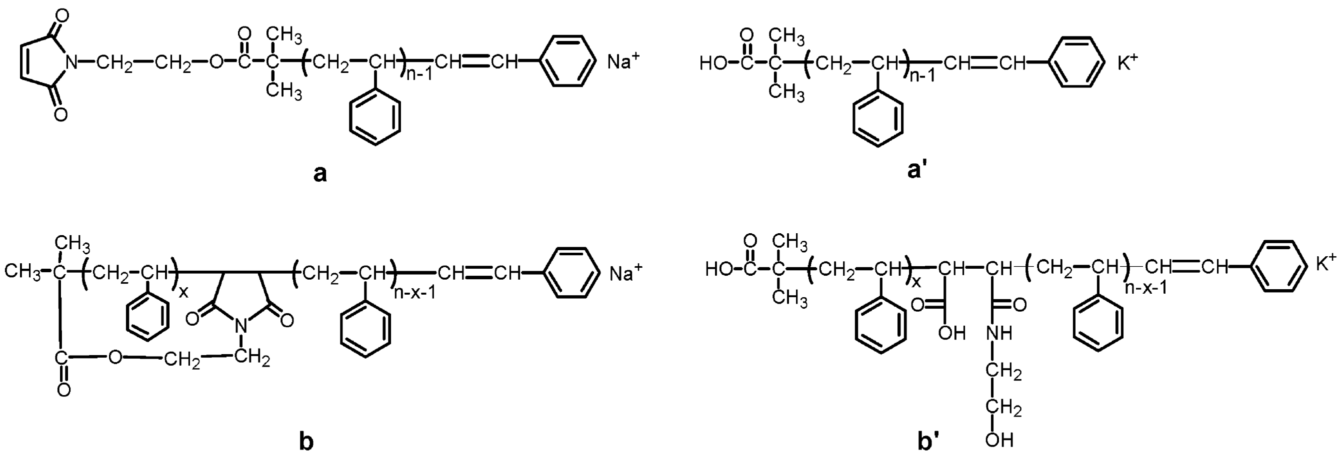


**Figure 10.** MALDI−TOF mass spectra of fraction Pl ($M_n$ = 1500, $M_w/M_n$ = 1.15) and its hydrolysis product.

**Scheme 3**



be made, but no peak from structure **a**′ was found as the same case observed in the analysis of hydrolysis products of the initially formed core in the former section. These results show that the structure of PI corresponds to structure **b**. This “6”-shaped polymer is supposed to be formed during the core forming stage. In early stage of ATRP in large excess of St, BiBEMI might initiate the polymerization of St to give a telechelic polySt oligomer besides the SCVP of BiBEMI and St. If more BiBEMI and St were added to the polymer, the core for star would be produced. However, in the case of the radical attacked the maleimide of its own in the end, cyclic ring was formed and further initiated polymerization of St which would give a “6”-shaped polymer.

**Characterization of the Star Polymer and Condition Optimization.** To prove the structure of main proportion with high molecular weight, the whole product was hydrolyzed under basic conditions due to the presence of ester groups in the star core originated from the inimer (Scheme 2). The representative GPC traces of the polymer and its hydrolysis product are given in Figure 11 (lines a and a′). The GPC trace obtained after hydrolysis is monomodal, and its polydispersity is low ($M_w/M_n$ = 1.11). It is interesting to notice that GPC shape and molecular weight of the hydrolysis product were almost the same as those of PI fraction in the polymer synthesized under such conditions. The results, together with the $^1$H NMR studies in first section, suggest that the main proportion is a star polymer with many polySt in low polydispersities covalently bonding to a core. No shoulder peaks observed also demonstrates no further branch point was formed during the homopolymerization of St once the core was produced. This is another proof that the cores are formed at the initial stage in a very short time.

**Table 3. Characterization of the Star Polymer**[a]

| $M_{w,GPC}$ (PDI) | $M_{w,SLS}$ | $M_{w,arm}$ (PDI) | arm no. | [$\eta$] | $g'$ (mL/g)[b] |
|---|---|---|---|---|---|
| 43000 (1.35) | 61170 | 5120 (1.12) | 12 | 0.077 | 0.24 |

[a] Fractionated from the product of the polymerization under the similar conditions as shown in Figure 1 with reaction time of 21.5 h. [b] $g' = [\eta]/[\eta]_L$, $[\eta]_L = 1.26 \times 10^{-4} M_{w,SLS}{}^{0.71} = 0.32$.

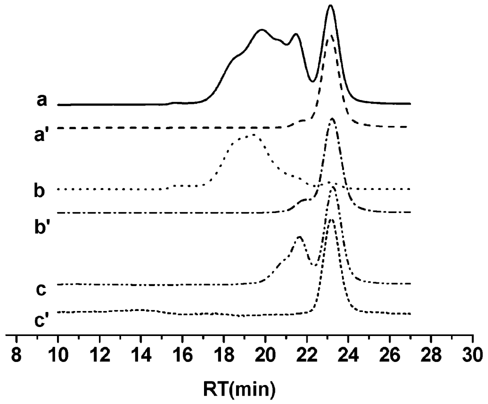


**Figure 11.** GPC traces of polymers and their hydrolysis product: a, polymer obtained under the same conditions as Figure 4 for 9.5 h; a′, hydrolysis product of a, $M_n$ = 6880, $M_w/M_n$ = 1.11; b, high molecular weight fraction from a, $M_n$ = 46 710; b′, hydrolysis product of b, $M_n$ = 6850, $M_w/M_n$ = 1.12; c, low molecular weight fraction from a; c′, hydrolysis product of c, $M_n$ = 6720, $M_w/M_n$ = 1.05.

It is known that coupling termination from two growing chains happens easily during the synthesis of a star polymer by ATRP from a core initiator. There are two types of possible coupling terminations, interstar and intrastar. One may notice that a shoulder peak in high molar mass region appears gradually from GPC traces in Figures 3 and 4. Because the terminations may couple two chains into one chain by C−C bond that is stable against hydrolysis and double the molecular weight, the star polymer was hydrolyzed to study the termination. Two fractions (lines b and c, Figure 11) with different molecular weights obtained by fractionation of the polymer using cyclohexane were hydrolyzed, respectively. GPC traces of their hydrolysis products are b′ and c′, respectively, in Figure 11. Although given from different fractions, the hydrolysis products almost had the same $M_n$ and $M_w/M_n$. A small leading hump was observed on the GPC curve (line b′) of the hydrolysis product from the high molecular weight fraction, while there was no such hump on that (line c′) of the low molecular weight fraction. The average molecular weight of the small leading hump was approximately twice of the main peak value. The results demonstrated that there was small extent of coupling termination during the polymerization at high St conversion.

To elucidate the arm number and the compact nature of the star polymer, one sample was fractionated from the product of the polymerization. Its molecular weights and intrinsic viscosity, [$\eta$], were determined as shown in Table 3. Its intrinsic viscosity, [$\eta$], was smaller than $[\eta]_L$ of linear polySt having the same molecular weight calculated by the equation $[\eta]_L = 1.26 \times 10^{-4} M_{w,SLS}{}^{0.71}$, and the $g'$ value ($[\eta]/[\eta]_L$ = 0.24) reveals its compact

**Table 4. Effect of Reaction Conditions on the Polymerization Products**

| entry | $[BiBEMI]_0:[St]_0:[CuBr]:[PMDETA]$ | $T$ (°C) | time (h) | solvent | $M_{n,star}$[a] | $M_{n,Pl}$[a] | Pl content (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | 1:50:0.5:0.5 | 80 | 7 | dioxane[c] | 9830 | 2190 | 29.8 |
| 2 | 1:50:0.5:0.5 | 45 | 30 | dioxane[c] | 8740 | 1610 | 19.2 |
| 3 | 1:50:1:1 | 23 | 72 | dioxane[c] | 7670 | 1510 | 18.4 |
| 4 | 1:20:1:1 | 45 | 48 | dioxane[d] | 18720 | 2620 | 14.8 |
| 5 | 1:20:0.5:0.5 | 45 | 48 | dioxane[d] | 5170 | 910 | 15.0 |
| 6 | 1:50:0.5:0.5 | 100 | 3.5 | anisole[c] | 13720 | 3170 | 31.6 |
| 7 | 1:50:1:1 | 23 | 72 | DME[c,e] | 7160 | 1450 | 20.7 |
| 8 | 1:50:0.5:0.5 | 45 | 19 | DME[c] | 4260 | 840 | 21.4 |
| 9 | 1:50:1:1 | 23 | 72 | bulk | 14440 | 2250 | 15.0 |
| 10 | 1:100:0.5:0.5 | 80 | 2.5 | bulk | 12630[f] | 2920[f] | 34.6 |

[a] Determined by GPC. [b] Obtained from GPC curves by comparing the area of the whole curve with that of Pl. [c] Solvent volume:St volume = 1:2. [d] Solvent volume:St volume = 1.3:1. [e] 1,2-Dimethoxyethane. [f] Peak value.

nature.[36] The star branched structure was further proven. Using the weight-average molecular weight of its hydrolysis product as the molecular weight of the arm, the average arm number is estimated to be 12 by comparing the absolute molecular weight $M_{w,SLS}$ of the star polymer and the molecular weight of the arm, $M_{w,arm}$.

Obviously, the polymer prepared by the present one-pot approach was a mixture of star polymer and Pl, although the content of Pl was low. To optimize the polymerization conditions and obtain a product with less Pl fraction, polymerizations were carrier out under various conditions. Table 4 shows that lowering the reaction temperature and using less excessive St can bring the expected results. Keeping the feed ratio of BiBEMI and St, the content of Pl fraction decreases from 29.8% to 19.2% to 18.4% when the polymerization temperature is lowered from 80 to 45 to 23 °C (see entries 1, 2, and 3 in Table 4). Comparing entries 3, 7, and 9, one can see that dioxane and 1,2-dimethoxyethane, as polar solvents, may facilitate the cyclization. The highest content of Pl fraction in entry 10 is due to the largest feed ratio of BiBEMI to St (1:100) and high reaction temperature (80 °C). When the feed ratio of BiBEMI to St changed from 1:50 to 1:20 (entries 2 and 5 in Table 4), the content of Pl fraction decreases from 19.2% to 15%. More feed of the catalyst seems have no apparent effect on the composition of the polymer (entries 4 and 5 in Table 4). The above results reveal that temperature, solvent, and feed ratio have influences on the ratio of P1 in the product. Such effects should play roles in the core formation stage. The radical in PS oligomer bearing maleimide end in early stage has two choices. One is to initiate the polymerization of the maleimide of another oligomer to give a potential branched core, i.e., intermolecular propagation. Another is to initiate the polymerization of the maleimide of its own in $\omega$-end to form a cycle, i.e., intramolecular interaction. The less polar solvent and lower temperature may favor intermolecular propagation to produce the core of a star instead of intramolecular interaction to give a molecular cycle.

## Conclusion

The one-pot approach to prepare star polymers based on ATRP of BiBEMI with a large excessive amount of St is presented. An intermediate as a multifunctional core is proven to be formed in situ at the initial stage of the polymerization in a short time by preferential consumption of BiBEMI; homopolymerization of the excessive St from the multifunctional cores as initiator can result in star polymers. Analysis of the hydrolysis products of the polymer formed in the initial stage by MALDI–TOF mass spectroscopy confirms the branched structure of the core. The star polymer bearing many arms with nearly the same length has been confirmed by hydrolysis studies. The main proportion of the reaction product is further proved to be a star polymer by comparing its intrinsic viscosity with that of linear polymer having the same molecular weight. The Pl fraction with small proportion, which coexisted with the star polymers, was found to be a "6"-shaped polySt. Lowering the reaction temperature and using less excessive St may get products with less Pl fraction. Although the star polymers prepared by the present developed way have relatively broad distributions, a simple approach in one pot is its main advantage and should be important in terms of practical application. The application of this one-pot approach to new systems is currently under investigation in order to get a better controlled star polymer and generalize this principle to other systems.

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